

LS coupling

1 The big picture

We start from the Hamiltonian of an atomic system:

$$\mathcal{H} = \sum_n \left[\frac{-\hbar^2 \nabla_n^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_n} \right] + \frac{1}{2} \sum_{n,m} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{nm}} + \mathcal{H}_{s-o} + \mathcal{H}_{h-f} + \mathcal{H}_B. \quad (1)$$

Here n runs over the electrons, \mathcal{H}_{s-o} is the spin-orbit hamiltonian, \mathcal{H}_{h-f} is the hamiltonian of the hyperfine interaction, and \mathcal{H}_B is the effect of any external magnetic field. An important point here is that we have neglected *many* contributions, some of which are not actually that small! For example:

- Finite nuclear mass.
- Finite nuclear volume.
- Relativistic velocity correction.
- Interaction of nuclear spin with external field.
- The fact that the nucleus has a range of internal states.

Some of these ignored terms genuinely are small - for instance, the interaction of the nucleus with an external field is always relatively unimportant. By contrast, the internal states of the nuclei are separated by enormous energies - so much so, in fact, that at the sort of energies we are concerned with in atomic physics we can just assume that nuclei are always in their groundstate.

Others, such as the finite nuclear mass and volume, and the relativistic velocity correction, are not small compared to the other perturbations. However, as I will explain at the end, they are not involved in splitting otherwise degenerate levels and hence are not important for the picture we build up here.

2 Central field approximation

The biggest terms in Equation 1 are the first three, which I have explicitly written out. These are not only impossible to solve analytically, they also include interactions between many bodies. So, in order to make any progress, we take as our first approximation \mathcal{H}_{cf} , where:

$$\sum_n \left[\frac{-\hbar^2 \nabla_n^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_n} \right] + \frac{1}{2} \sum_{n,m} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{nm}} = \sum_n \left[\frac{-\hbar^2 \nabla_n^2}{2m_e} + U(r_n) \right] + \mathcal{H}_{residual} = \mathcal{H}_{cf} + \mathcal{H}_{residual} \quad (2)$$

The idea is to incorporate as much of the electronic interaction as possible into the central field $U(r_n)$, leaving only a relatively small multi-body term. If we neglect this multi-body term to first order, then the Schrödinger equation can be separated and solved for individual electrons. Assuming we have some numerical way of finding $U(r_n)$ and solving for the single-electron eigenfunctions, we will be able to construct product eigenstates of the form:

$$|\Psi\rangle = |\psi_a(r_1, \chi_1)\rangle |\psi_b(r_2, \chi_2)\rangle |\psi_c(r_3, \chi_3)\rangle \dots \quad (3)$$

where the individual states are solutions to the separated equations:

$$\left[\frac{-\hbar^2 \nabla^2}{2m_e} + U(r) \right] |\psi_i(r, \chi)\rangle = E_i |\psi_i(r, \chi)\rangle. \quad (4)$$

Here χ represents spin degrees of freedom, which at this stage do not influence the energy. The total energy of $|\Psi\rangle$ is simply a sum of all the individual energies. Although this is a perfectly good eigenstate of H_{cf} , it doesn't obey exchange symmetry, which states that for fermions such as electrons *any* state *must* be antisymmetric under exchange any pair of particles. We can antisymmetrize $|\Psi\rangle$ using a Slater determinant:

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\psi_a(r_1, \chi_1)\rangle & |\psi_b(r_1, \chi_1)\rangle & \dots \\ |\psi_a(r_2, \chi_2)\rangle & |\psi_b(r_2, \chi_2)\rangle & \dots \\ \dots & \dots & \dots \end{vmatrix} \quad (5)$$

This antisymmetrization process means that for n electrons, n distinct eigenstates must be used – this is a restatement of the Pauli exclusion principle. Often we can get lazy, and say one electron *is in* state a , and another in state b , but we should always remember that in truth there is no distinction between electrons, and in our representation of quantum mechanics this manifests itself as antisymmetrized rather than product wavefunctions.

So, we can say which state the system is in (at this level of approximation) simply by writing down the quantum numbers which label each single-electron state that is occupied. But what are these quantum numbers? From what we know about Hydrogen and central fields, these will be the principle quantum number n , orbital angular momentum l , z-component of orbital angular momentum m_l and the z-component of electron spin m_s . However, as m_l and m_s have no effect on the energy, these are suppressed and so:

$$1s^2 2s^2 2p^3 \quad (6)$$

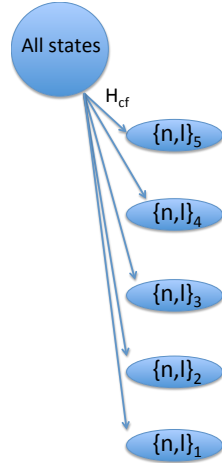


Figure 1: Effect of turning on the Hamiltonian \mathcal{H}_{cf} . With $\mathcal{H} = 0$, all states are eigenstates with zero energy, and I have grouped them together in the top left. Turning on \mathcal{H}_{cf} chooses certain states as eigenstates and splits these previously degenerate states into groups of states which are labelled by their configuration. But remember, there is still degeneracy with respect to m_l and m_s for a given configuration.

means 2 electrons in $n = 1$, $l = 0$ (remember l states are labelled by letters; s for $l = 0$), 2 electrons in $n = 2$, $l = 0$ and 3 in $n = 2$, $l = 1$. This is known as the configuration level of description. The effect of ‘turning on’ \mathcal{H}_{cf} is shown diagrammatically in Figure 1.

3 Residual Electrostatic

We now have a series of perturbations which we must consider in order of their importance. In lighter atoms, the next most important term is the residual electrostatic interaction – the assumption that this is greater than the spin-orbit interaction is really the starting-point of the ‘LS coupling’ scheme. For a discussion of this assumption, see Foot or a similar text.

We wish to apply perturbation theory to find out how the residual electrostatic interaction affects our energies. We know, however, that if we apply perturbation theory to degenerate eigenstates, we must choose a basis for our degenerate subspace that diagonalizes the perturbing Hamiltonian. This prevents the second-order terms from diverging (see Gasiorowicz or Binney).

Our subspace is degenerate with respect to the m_l and m_s of the states in the partially-filled n, l shells. Unfortunately these states do not diagonalize the perturbing Hamiltonian within the degenerate subspace, as the \mathbf{L}_z do not commute with the residual electrostatic perturbation.

However, the perturbing Hamiltonian *necessarily* commutes with $\mathbf{L} = \sum_i \mathbf{l}^i$ and \mathbf{L}_z , as the total orbital angular momentum of electrons is not coupled to any other torque. Similarly, $\mathbf{S} = \sum_i \mathbf{s}^i$ and \mathbf{S}_z commute with the perturbation. So if we choose the basis of our degenerate

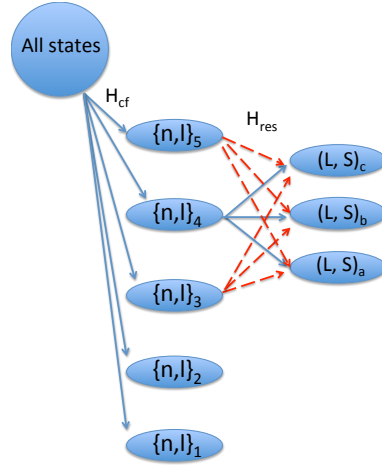


Figure 2: Effect of turning on the Hamiltonian \mathcal{H}_{res} . Configurations are split into terms depending on L and S - note the small configurations to the terms from other configurations, shown in red. I have only shown contributions from adjacent configurations for convenience – don't read any physics into this. These terms are still degenerate with respect to M_l and M_s .

subspace to be states with well defined quantum numbers L , S , M_l and M_s , we should be fine.

So the net effect of the perturbation is to split the configurations into terms of well defined L and S . These terms are still degenerate with respect to M_l and M_s , as there is no preferred direction for the atom. Note also that, if we were to consider higher orders of perturbation theory, the effect of \mathcal{H}_{res} would be to mix configurations a small amount. What I mean here is that \mathcal{H}_{res} not only changes the energies of the eigenvalues, but the eigenstates themselves – you can see the second order correction to wavefunctions in Gasiorowicz or Binney. Referring to Figure 2, the result is that the $(L, S)_b$ term from the $\{n, l\}_4$ configuration has small components from states with the same L and S but other configurational wavefunctions – these small contributions are shown by the dashed red lines in Figure 2. Whilst these contributions are small, it is still meaningful to talk about the configuration of a given term, even though truthfully a term will contain small contributions from a number of configurations. These contributions remain small as long as the energy splitting of the unperturbed states is large compared to the perturbative interaction.

4 Spin-orbit interaction

I'm not going to go into details about the form of the interaction here, refer to the standard textbooks for that. The point is that we have finally coupled orbital angular momentum and spin operators. The end result is that M_l and M_s are obviously not good quantum numbers of

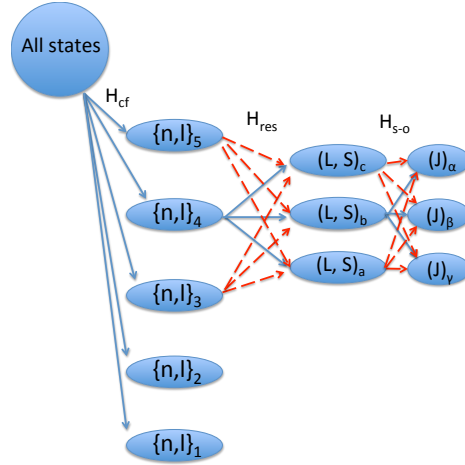


Figure 3: Effect of turning on the Hamiltonian \mathcal{H}_{s-o} . Terms are split into terms levels of different J - note the small contributions to the levels from other terms, shown in red. I have only drawn two other terms contributing for convenience, but all other terms will contribute in principle, even from other configurations. These levels are still degenerate with respect to M_J .

the perturbation, so we use eigenstates of the total angular momentum \mathbf{J}^2 and its z-component if we are to diagonalize within the degenerate subspace (as we must). Again, there is no special direction for the atom, so eigenstates must be degenerate with respect to M_J , and split the terms into levels according to J .

Note that again, although we have diagonalized within the *degenerate subspace*, the perturbation will still connect states to other states within terms of different L and S (and, to a lesser extent, different configurations). Whilst the spin-orbit interaction is small, the consequences are small and so it is still reasonable to use L and S as good quantum numbers (as you do when you calculate ΔE according to the method presented in lectures). As the spin-orbit interaction becomes comparable to the residual electrostatic, however, this ceases to be the case. This is shown diagrammatically in Figure 3.

5 Hyperfine interaction

Now we start to notice that the nucleus has a spin, I ! Should we go back and do everything again? Of course, there is no need – nuclear spin operators commuted with all previous perturbations. Therefore we just need to say that at each previous stage the nuclear spin and electron wavefunctions appeared as a product, with the nuclear spin states in any orthogonal basis.

Again, I am not that concerned with the details of the interaction, but we know that it couples nuclear spin \mathbf{I} and the total electronic angular momentum \mathbf{J} . Our levels are degenerate

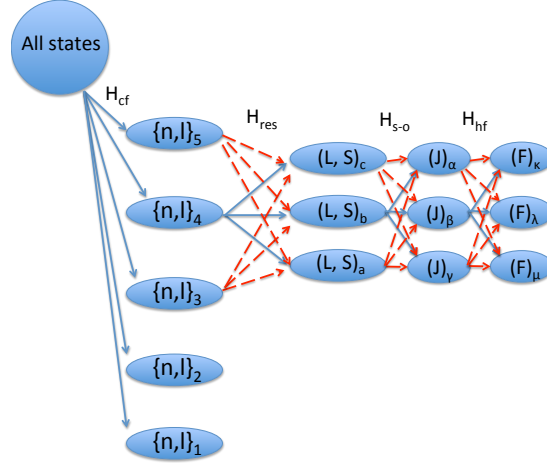


Figure 4: Effect of turning on the Hamiltonian \mathcal{H}_{hf} . Levels are split into states depending on F - note the small contributions to the states from other levels, shown in red. I have only drawn two other levels contributing for convenience, but all other levels will contribute in principle, even if they are in other terms and configurations. These states are still degenerate with respect to M_F .

with respect to M_J and M_I , but \mathbf{J}_z and \mathbf{I}_z do not commute with the perturbation. There is no external torque on the atom, however, so if we define $\mathbf{F} = \mathbf{J} + \mathbf{I}$ then we know F and M_F will be good quantum numbers, with the levels split according to F and degenerate with respect to M_F . Once more, different J -levels will actually be connected by the perturbation, but the connection will be weak and so it is meaningful to talk about the resultant states having well-defined L , S and J – see Figure 4.

6 Magnetic interaction

External magnetic fields would like to couple to the orbital angular momenta and spin of electrons. However, if the magnetic hamiltonian is smaller than the spin-orbit interaction, m_l and m_s are not good quantum numbers of the eigenstates prior to perturbation application. The net effect is that the magnetic field will couple to whichever angular momentum is well-defined, and split the degenerate eigenstates according to M_L and M_S , M_J or M_F , depending on how strong it is. Figure 5 demonstrates the effect for a magnetic field that is weaker than the hyperfine structure, so states of well-defined F are split according to M_F . Once again, there is some connection with states with different F values, but provided the magnetic field is small enough the consequences are small.

An important point to note here is that when you apply the vector model, you get hamiltono-

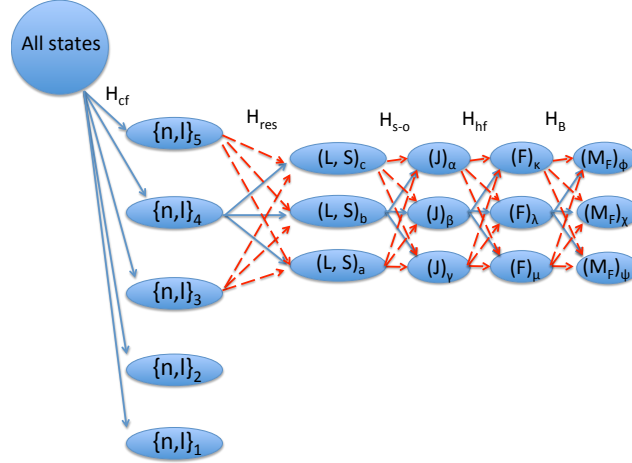


Figure 5: Effect of turning on the Hamiltonian \mathcal{H}_B , for a magnetic interaction small compared to hyperfine structure. Degenerate states are split into states depending on M_F - note the small contributions to the states from other values of F , shown in red. Again, in reality small contributions will be made from all other degenerate groups of states – even those associated with different levels, terms and configurations – not just the immediate neighbours. Assuming that at each stage of the process the new Hamiltonian has a significantly smaller effect than the previous ones, then it is reasonable to associate the quantum numbers $\{n, l\} = \{n, l\}_4, L = L_b, S = S_b, J = J_\beta, F = F_\lambda, M_F = (M_F)_\chi$ with the middle state on the far right. However, it should be remembered that this is only an approximation!

nians which look like:

$$\mathcal{H}_{s-o} = \beta_{LS} \mathbf{L} \cdot \mathbf{S} \quad (7)$$

and

$$\mathcal{H}_{hf} = A_J \mathbf{I} \cdot \mathbf{J} \quad (8)$$

These look like they commute with \mathbf{L}^2 , \mathbf{S}^2 and \mathbf{I}^2 , \mathbf{J}^2 respectively. If this was the case, there would be strictly zero connection between different L, S terms when the spin-orbit perturbation was applied, and similarly no connection between different J levels when hyperfine perturbations are considered. However, the vector model is only approximate, and in essence assumes that there is no connection in deriving the form of the perturbation. So the true perturbing hamiltonians would lead to the kind of connections shown by the red dashed lines in my figures.

7 What about the neglected perturbations?

If you remember, I said that corrections such as the relativistic velocity perturbation and finite nuclear size were unimportant in splitting otherwise degenerate states. Why is this? The important thing to note is that they do not involve any coupling between different electrons, and do

not act on the spin degrees of freedom. Hence they only care about the configuration part of the wavefunction. They will therefore not split terms, levels or hyperfine levels, but contribute the same shift to each. Furthermore, they will not prevent L , S , M_L , M_S , J , M_J , F and M_F being good quantum numbers, and so all the arguments we have applied will still hold even if these perturbations are taken into account.

8 Violation of selection rules

In the course we have considered selection rules for electric dipole radiation. Many of these can be broken – what is the mechanism for this? Sometimes, transitions can proceed via other mechanisms – *eg.* magnetic quadrupole radiation. But in other cases, electric dipole radiation does appear to violate its own selection rules – how is this possible?

As an example, consider the selection rule $\Delta S = 0$. This essentially arises because electric dipole radiation does not couple to spin degrees of freedom. You have seen in the first tutorial that this rule is broken in Hg – does this mean that different spin states can be coupled by the electric dipole interaction?

It does not. It signifies that our labelling of states with a certain value of S is not perfectly accurate – a given state predominantly has one S value, but also contributions from others due to the spin-orbit interaction (see Figure 3). The stronger the spin-orbit interaction relative to the residual electrostatic, the worse our assumption that states have a well-defined S becomes. Eventually, when $\mathcal{H}_{s-o} \sim \mathcal{H}_{res}$, the approximation loses any validity. This is where LS coupling itself loses its validity.

So in general, when a selection rule is ‘violated’, what we have really found is that the quantum numbers we have applied to the state aren’t exactly true. Violations become stronger as the description in terms of a given quantum number becomes less accurate.